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## On the pore water chemistry effect on spectral induced polarization measurements in the presence of pyrite

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### ABSTRACT

In order to expand the application of the induced polarization (IP) method as a technique for monitoring metallic mineral dissolution and precipitation mechanisms, we studied the effects of variations in pore water chemistry on the spectral induced polarization (SIP) response of a mixture of silica-sand and pyrite particles in the laboratory. We investigated the dependence of the SIP response on both pore water conductivity and pH for various chemical compositions: redox-passive (P) versus redox-active (A) ions, using  $\text{CaCl}_2$  as P-ions, and  $\text{FeSO}_4$  and  $\text{FeCl}_3$  as A-ion brines. The effect of pore water chemistry was evaluated by means of a recently proposed volumetric specific capacitance model. The SIP response (IP-effect) was primarily determined by the pore water conductivity and the specific capacitance was only weakly dependent on the chemical composition and  $\text{pH}_w$ . We found that the specific capacitance varies to first order over a limited range and approximates a single value ( $\approx 302 \text{ F m}^{-3}$  in average). However, variations in the specific capacitance as a function of active versus inactive ion chemistry might be important to consider when using IP to monitor specific mineral dissolution and precipitation processes.

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### 1. Introduction

Studies on the induced polarization phenomenon (IP-effect) associated with metallic particles have increased in recent years. These include investigations on biogeochemical transformations (Flores-Orozco et al., 2011; Ntarlagiannis et al., 2005; Personna et al., 2008; Slater et al., 2007; Williams et al., 2005, 2009), oxidation–reduction (redox) reactions (Hubbard et al., 2014; Placencia-Gómez et al., 2013), mine tailings and acid mine drainage characterization (Campbell and Horton, 2001; Placencia-Gómez et al., 2015; Vanhala et al., 2005; Yuval and Oldenburg, 1996), monitoring of reactive iron barrier performance (Slater et al., 2005, 2006; Wu et al., 2005); and characterization of the polarization properties of different metal minerals (Abdel Aal et al., 2014; Gurin et al., 2013, 2015; Zhdanov et al., 2012) and nanoparticles (Joyce et al., 2012; Flores-Orozco et al., 2015). Such studies mainly focus on the role of the metal content (total weight or volume fraction percentage) and physical (textural) properties such as the metallic particle grain size and surface area on the spectral induced polarization (SIP) response. In contrast, relatively few studies have examined the significance of the physical and chemical characteristics of the metal–electrolyte interface controlling the IP-effect (e.g., Flekkøy, 2013; Gurin et al., 2015;

Hubbard et al., 2014; Merriam, 2007; Placencia-Gómez and Slater, 2014) in such systems.

Models to describe the electrochemical characteristics of the IP-effect at the metallic mineral surface–electrolyte interface, i.e., in the electrical double layer (EDL), are still lacking. The only electrochemical-based IP model is the approach developed by Wong (1979), which provides a link to the mechanistic understanding of the SIP response associated with oxidation–reduction processes and initially focused on disseminated metal ores. The model of Wong incorporates significant simplifications due to the complexity of the electrochemical oxidation–reduction reactions at the metal–electrolyte interface involved in the IP phenomenon. Even with such simplifications, the Wong model still contains eight parameters with some of them dependent on others. For instance, (1) the diffusion coefficient ( $D$ ) is considered the same for both the redox-active and redox-passive ions in the electrical double layer (EDL), whilst the passive/active ion concentration ratio is considered very large and the redox-active ions are engaged in diffusive mass transport only; (2) the equilibrium current density ( $i_0$ ) associated with the transfer of charge ( $e^-$ ) at the metal–electrolyte interface is complicated to define accurately due to the various possible redox reactions, i.e.,  $i_0$  will depend on every specific redox reaction between ions and type of metallic mineral (Angoran and Madden, 1977; Klein and Shuey, 1978). Consequently,  $i_0$  is directly related to the magnitude of the electrochemical reaction modelling parameters ( $\alpha, \beta$ ), and thus to the specific surface conductance of metallic particles, accounting for the interfacial charge storage or capacitive properties; (3) the parameter defining the distance

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from the metallic mineral surface to the outer Helmholtz plane ( $l$ ), i.e., the thickness of the Stern layer, directly affects the  $\alpha$  parameter and thus the specific surface conductance.

Placencia-Gómez and Slater (2014) found that the Wong model in some cases shows an imperfect fit to experimental data obtained on synthetic mixtures of sand with pyrite or pyrrhotite over the frequency range 0.1–10,000 Hz, although it fits relatively well around the peak relaxation frequencies. Gurin et al. (2013, 2015) found a quadratic dependence of the relaxation time ( $\tau$ ) on the grain (metallic particles) size, whereas the model of Wong suggests two relationships: quadratic for large particle radii and linear for small radii. Furthermore, Gurin et al. (2015) found an inconsistency in the relaxation time ( $\tau$ ) – pore water conductivity ( $\sigma_w$ ) relationship between the experimental data and the predictions of the Wong model (Fig. 6 of Gurin et al. (2015)). These discrepancies likely reflect the simplifications of the Wong model as discussed above.

In the absence of mechanistic models, Gurin et al. (2015) proposed a semi empirical model to characterize the IP signatures of disseminated metallic particles in terms of relaxation time  $\tau$ , developing a simple equation describing the dependence of  $\tau$  on the radius of metallic particles ( $r^2$ ) and the pore water conductivity ( $\sigma_w$ ), via a volumetric specific capacitance term ( $a$ ), considered to represent the chemical (and possibly mineralogical) characteristics of the metallic mineral–electrolyte interface. However, these authors recognized a need for additional work to examine the role of the surface chemistry on the specific capacitance term.

In this work, we investigate the pore water chemistry effects on the SIP response of a pyrite-sand (*py-sand*) mixture, considering the role of redox-passive (inactive) ions,  $\text{Ca}^{2+}$  ( $\text{CaCl}_2$ ), versus redox-active ions,  $\text{Fe}^{3+}$  ( $\text{FeCl}_3$ ) and  $\text{Fe}^{2+}$  ( $\text{FeSO}_4$ ). We focus on how the volumetric specific capacitance parameter ( $a$ ) depends on pore water chemistry and the critical role of  $\text{pH}_w$  (between pseudo-neutral and acidic conditions). Given the complexity of the electrochemical processes involved in generating the IP-phenomenon, the use of empirical (or semi-empirical) models, incorporating a specific capacitance at the metal–electrolyte interface could substantially facilitate the interpretation of the IP response in soils containing disseminated metals. This laboratory work could contribute significantly to the development of the IP method for characterizing mine tailings deposits and the development of acid mine drainage discharges, as well as to expand applications of IP method where monitoring the dissolution of metal sulphides (metal mass content) under acidic conditions is required: one example is the bioleaching process of both low-grade sulphide ore and waste heaps.

## 2. Induced polarization background and models

The SIP response of saturated porous materials (e.g., soils) can be represented in terms of a frequency-dependent complex conductivity ( $\sigma^*$ ) with real ( $\sigma'$ ) and imaginary ( $\sigma''$ ) components. In polar form  $\sigma^*$  is expressed as,

$$\sigma^*(\omega) = |\sigma(\omega)| \exp^{i\varphi(\omega)}, \quad (1)$$

where  $i$  is the imaginary unit ( $i = \sqrt{-1}$ ). The magnitude  $|\sigma(\omega)|$  and phase angle ( $\varphi(\omega)$ ) are related to the real and imaginary conductivity frequency-dependent components by,

$$|\sigma(\omega)| = \sqrt{(\sigma'(\omega))^2 + (\sigma''(\omega))^2} \quad (2)$$

and,

$$\varphi(\omega) = \tan^{-1} \left( \frac{\sigma''(\omega)}{\sigma'(\omega)} \right), \quad (3)$$

where  $\varphi \approx \sigma''/\sigma'$  for small values. The real conductivity component ( $\sigma'$ ) depends partly on the electromigration of charge associated with

ions in the pore space, i.e., the electrolytic pore water conductivity ( $\sigma_w$ ) which dominates the bulk conductivity ( $\sigma_b$ ) of granular porous media in the absence of metallic particles. In the presence of disseminated metallic particles, the  $\sigma'$  will be also dependent on the in-phase (real) component ( $\sigma'_{surf}$ ) of surface conductivity ( $\sigma^*_{surf}$ ) associated with the development of the EDL of such metallic particles. Although surface conductivity also exists for non-metallic minerals, the effect might be enhanced in metallic minerals due to the large amount of charge per unit surface resulting from the tendency of metals to support electronic conduction. Furthermore, unlike non-metallic minerals, the surface electrical properties of metallic particles can facilitate electrochemical redox reactions, resulting in a charge-transfer or faradaic current ( $i_{ct}$ ) between the metallic mineral and the electrolyte at surface sites where redox active ions (i.e., electrons acceptors) have accumulated as illustrated in Fig. 1b. The faradaic conduction path provides an additional charge transport process in the EDL (Merriam, 2007), giving rise to a charge-transport conductivity ( $\sigma^*_{ct}$ ) in addition to the surface conductivity ( $\sigma^*_{surf}$ ), where the latter accounts for the ionic space charge which is not engaged by redox reactions with the metallic mineral, i.e., a non-faradaic conduction path. Thus, when redox reactions take place at the interface, the real conductivity will be determined by the superposition of different conduction paths  $\sigma' = f(\sigma_w, \sigma'_{surf}, \sigma'_{ct}, \sigma_e)$ , where  $i_{ct}$  may drive electronic conduction ( $\sigma_e$ ) through isolated metallic particles.

The imaginary conductivity ( $\sigma''$ ) represents the capacitive properties of both non-metallic and metallic particles associated with the net surface charge density or charge storage on the grain surface. In the presence of metals,  $\sigma''$  strongly depends on the physical properties of the metallic mineral and the electrochemical characteristics of the metallic mineral surface–electrolyte interface; see e.g., Slater et al. (2005), Wu et al. (2005), Hubbard et al. (2014) and Placencia-Gómez and Slater (2014), respectively. The  $\sigma''$  is defined as the quadrature component of surface conductivity  $\sigma'' = \sigma''_{surf}$ , which in the case of faradaic currents would comprise both non-faradaic and faradaic contributions, yielding  $\sigma'' = f(\sigma''_{surf}, \sigma''_{ct})$ . This polarization term is strongly sensitive to the amount of available specific surface area of non-metallic and/or metallic minerals (see e.g., Lesmes and Frye, 2001; Slater et al., 2006; Weller et al., 2010; Wu et al., 2005), and considered weakly dependent on pore water conductivity in non-metallic minerals (Lesmes and Frye, 2001). For the experimental conditions in this work (Section 4), the specific metallic surface area is proportional to the metal content in the mixtures; given that the sample mixtures are identical in each column we assume that the contribution of metal content (or metallic surface area) to the measured SIP response is the same for all columns. Therefore, the contrasts in the SIP measurements and modelling parameters will be primarily attributed to the chemical characteristics of pore water, which is our main interest here.

In this work, we pay particular attention to the relationship for the relaxation time recently proposed by Gurin et al. (2015) (their Eq. 12). This model describes the total relaxation time ( $\tau$ ) in terms of the metallic grain radius ( $r$ ) and the pore water conductivity ( $\sigma_w$ ),

$$\tau = a \frac{r^2}{\sigma_w} = ar^2 \rho_w \quad (4)$$

where  $\rho_w$  ( $1/\sigma_w$ ) is the pore water resistivity in Ohm m, and  $a$  is defined as the volumetric specific capacitance in a volume of rock in  $\text{F m}^{-3}$ , presumed to depend on the surface chemistry, texture and mineralogy. This empirical model was experimentally determined from time-domain IP measurements on composite samples of metallic minerals mixed with silica sand where the polarization signatures were characterized using a Debye decomposition (DD) approach (Tarasov and Titov, 2007). Gurin et al. (2015) examined how this model fits the variations of the time constant as a function of the metallic particle radius, particle concentration and fluid salinity. They restricted their analysis to pore fluids composed of redox-inactive  $\text{Na}^+$  and  $\text{Cl}^-$  ions

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